

Angular Distributions of Molecular-Field and Spin-Orbit Split Core Levels of Sulfur 2p Photoemission in OCS: A Sensitive Probe of the Molecular Environment

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INTRODUCTION

The photoelectron spectra (PES) of inner-shell electrons in molecules can be subtly perturbed by the molecular environment in which they are embedded. Large spin-orbit splittings of core orbitals in heavier atoms are commonly observed in molecular PES, but the much smaller molecular field splittings require high energy resolution for their experimental observation.

The angular distributions of photoelectrons are sensitive probes of the potential field experienced by the departing electrons. In the case of molecules, the angular distributions of electrons leaving inner-shell orbitals can be altered due to scattering from neighboring atoms into many partial waves, and they are also influenced by molecular vibration and rotation. To date, only experiments on spatially oriented diatomic molecules have been able to probe the molecular (body-frame) environment in angle-resolved photoemission studies [1]. In such experiments, the photoelectrons are detected in coincidence with ionic fragments of the molecule at selected angles. It is, however, very difficult to obtain sufficiently high count rates together with high energy resolution in such coincidence experiments.

EXPERIMENT

Non-coincidence PES measurements of angular distributions, with their high count rates and high energy resolution, can provide an alternative to coincidence techniques by fully resolving the effects of spin-orbit and molecular-field splittings. We measured angle-resolved PES of sulphur 2p of the carbonyl sulphide (OCS) molecule with completely resolved spin-orbit, vibrational, and molecular field splittings, and provided a supporting theoretical interpretation for the experimental anisotropy parameters [2].

The experiment was carried out at beamline 10.0.1. The photon beam, monochromatized by a spherical grating monochromator operating at about 10,000 resolving power, interacted with the target molecular gas in an experimental station equipped with a Scienta SES-200 electron energy analyzer designed for angle-resolved gas-phase electron spectroscopic measurements. The analyzer, which is rotatable in the plane perpendicular to the propagation direction of the linearly polarized incoming photon beam, was set to provide an electron energy resolution of about 25 meV, resulting in an overall instrumental broadening of 30 to 35 meV.

Figure 1 shows the S 2p PES, excited by 191 eV photons, taken at different angles relative to the polarization plane. The molecular field splitting into three different components (marked by A, B and C) as well as the vibrational splitting are clearly resolved. Spectra similar to Fig. 1 show that the angular distributions of the components B and C are different over broad photon energy range, an effect specific to the molecular environment.

THEORY

The origins of the spectral features reported in Fig. 1 can be understood quantitatively on basis of the specific forms of the wave functions describing the spin-orbit, vibrational, and molecular-field split core-excited ionic states of good total electronic angular momentum along the internuclear axis. The measured $\beta(B)$ and $\beta(C)$ values are shown by theoretical analysis to provide the anisotropy parameters $\beta(2p\sigma)$ and $\beta(2p\pi)$, which are generally inaccessible separately due to the near degeneracy of these inner-shell ionic states. The latter values, furthermore, provide body-frame information in the absence of explicit sample alignment.

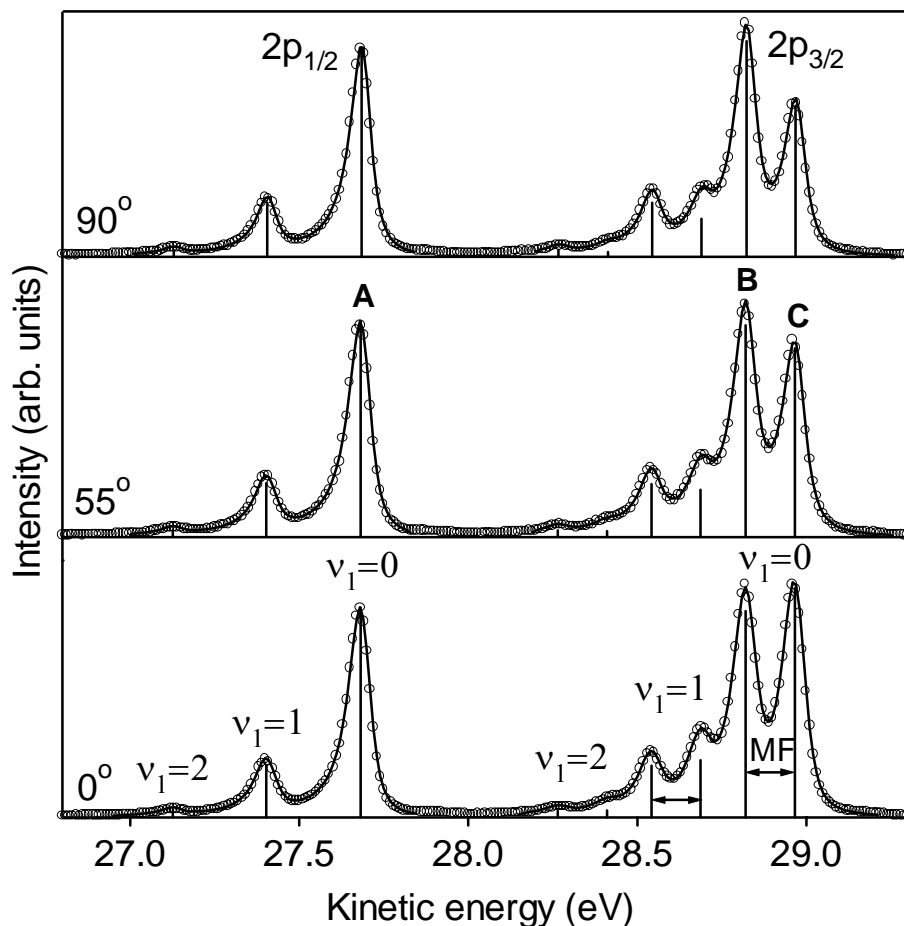


Figure 1. Sulphur 2p photoelectron spectra of the OCS molecule excited by 191 eV photons. The molecular field split components are marked by A, B and C.

REFERENCES

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